NEAR ULTRAVIOLET SPECTRA OF BENZENE
IN FROZEN CYCLOHEXANE SOLUTIONS

by

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B. S., Goshen College, 1963

A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1967

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INTRODUCTION

The benzene molecule has been studied in great detail. From ultraviolet, infrared, and Raman studies, the ground state vibrational frequencies, a number of the singlet electronic excited state energies, and the first electronic excited triplet state energy are well known.

Recent studies have dealt with benzene in solid solutions at low temperatures. When excited with radiation of wavelength between 2300Å and 2650Å, benzene in solid solutions at low temperatures fluoresces and phosphoresces. Benzene will form a mixed crystal in a few cases where the solvent is carefully chosen. When mixed crystals are formed, the absorption and emission spectra are well resolved and one can study the vibrations that are coupled to the electronic transitions.

Cyclohexane is an example of a solvent that forms a mixed crystal with benzene. It also does not absorb or emit in the region of interest. Because of these two factors, cyclohexane has been used commonly as a solvent for benzene. Another property of cyclohexane, which sometimes has not been recognized, is that cyclohexane undergoes a solid-solid phase transition at 186°K. The phase above 186°K will be called phase H, and the stable phase below 186°K will be called phase L (H corresponds to high temperature and L corresponds to low temperature.). With very rapid freezing, these two crystal forms of cyclohexane are both present at 77°K. The presence of the phases H and L results in a doubling of the absorption, fluoresence, and phosphorescence bands.

Sponer, Kanda, and Blackwell[1] analyzed the phosphorescence of benzene in cyclohexane for a sample that was frozen rapidly. In their analysis, they used three different (0, 0) levels. Two of these correspond to the two crystalline forms of cyclohexane. This was shown by Spangler and Sponer[2], who studied the absorption and phosphorescence spectra of benzene in cyclohexane. They varied the sample freezing rate and found that the relative amounts of the absorption and emission for phase H and phase L varied. Slow freezing give all of phase L, while rapid freezing resulted in mostly phase H. An analysis of the absorption bands was made.

A partial analysis of the fluorescence has been made by Leach and Lopez-Delgado[3]. Leach et al.[4] have also studied the effect of temperature on the spectrum of benzene in cyclohexane and observed the shift in wavelength when the crystal makes the transition from phase L to phase H. This had previously been observed by Spangler and Sponer[2] in the absorption.

The lifetime of the first triplet state in benzene has been measured in a number of solvents, and Hirayama[5] has recently measured it in cyclohexane. Thompson[6] gives 18 sec in CH_4, 10 sec in Ar, 1.8 sec in Kr, 0.04 sec in Xe at 4.2°K, and Wright, Frosch, and Robinson[7], give 16 sec in CH_4, 16 sec in Ar, 1 sec in Kr, and 0.07 sec in Xe.

Further study is needed in several areas. Sponer, Knada, and Blackwell[1] indicated that the relative intensity of the phosphorescence from phase H and phase L was a function of the concentration. Spangler and Sponer[2] showed that the relative amounts of absorption by the two phases depended on the freezing rate. Further study is needed in which the relative intensities in all the regions can be simultaneously observed with variation of both the freezing rate and the concentration. Also, Hirayama's lifetime study with concentration as a variable shows an anamolous effect, which he suggested might somehow be related to the two crystal forms of cyclohexane.

In the experiments to be discussed in this paper, the freezing rate and the concentration of the samples have been varied. The data was obtained by taking plates which show simultaneously absorption, fluorescence, and phosphorescence. Also, pictures have been taken of oscilloscope traces which show the intensity decay of the phosphorescence after the exciting radiation has been cut off. From these pictures, the lifetime of the phosphorescence can be calculated. The lifetime has also been studied as a function of concentration and freezing rate.

THEORY

The primary area of study of this thesis concerns the effects of environment on the spectrum of benzene. A basic understanding of the processes involved in absorption and emission is needed, but a detailed analysis using group theory to determine selection rules for transitions will not be carried out. Two references on theory are Tinkham[8] and Murrel[9].

Electronic States

Benzene absorbs and emits in the near ultraviolet region of the spectrum. Benzene has three electronic states in this region; and these are shown in Fig. 1 along with thier approximate energies. The electronic energy levels depend slightly on the environment around the benzene molecule. Transitions between the S_1 and S_0 and between the T_1 and S_0 are seen in our experiments. When the benzene molecule occupies a site in a crystal, the spectra related to these transitions are shifted to the red in comparison to the gaseous state by approximately 200-300 cm^{-1}.

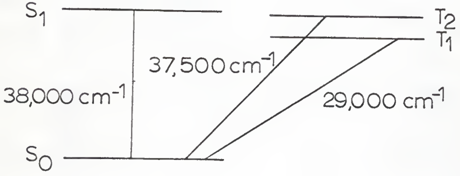


Fig.1

Vibronic States

Coupled to the electronic transitions are vibrational transitions. The most common vibration present is the totally symmetric breathing vibration (992 cm^{-1} in the ground state) in which all the atoms are moving in and out together. The various vibrational frequencies for the ground state are quite well known from infrared, Raman, and the near ultraviolet spectra. The vibrational frequencies are somewhat different for the different electronic states, although they are changed only slightly, if at all, by changing the environment around the molecule. The purely electronic transitions S_1 to S_0 and T_1 to T_0 are forbidden by symmetry in the free molecule (the latter by spin also), and various asymmetrical (e_g^+) vibrations are active in making the transition allowed.

Lattice Vibrations

In a crystal, lattice vibrations can also be present. The lattice vibrations couple to the electronic transitions to broaden the bands. Their energy is of the order of 10 cm^{-1} to 150 cm^{-1}.

Jablonski Diagram

The basic transitions in benzene can be seen by looking at the Jablonski diagram in Fig. 2. The diagram shows energy levels arising from the possible electronic energy levels and vibrational levels. For low temperatures, all the absorption processes will normally start from the lowest vibrational level in the ground electronic state. This absorbed energy puts the molecule into an excited electronic state and usually also an excited vibrational state. The transition probability to the S_1 state is

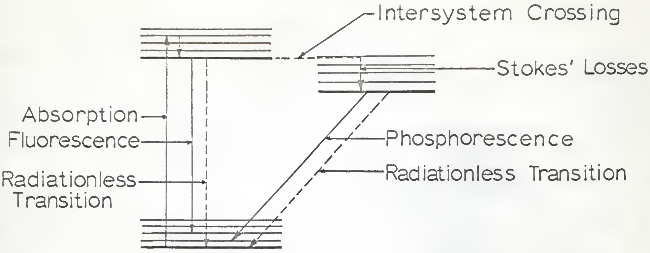


Fig. 2

approximately 10^6 times that to the T_1 state, so the absorption observed is normally S_0 to S_1. The vibrational energy acquired in the absorption process is lost rapidly to the crystal surrounding the molecule in radiationless transitions called Stoke's losses. This leaves the molecule in the lowest vibrational level of the first excited state. For mixed crystals with low concentrations of benzene, there are three processes for depopulating this state. First, radiation can be emitted in a transition to the ground electronic state. This process is called fluorescence. Second, a radiationless transition can take place to the ground state. Third, intersystem crossing can occur, which means the molecule changes from a spin of 0 to a spin of 1. An equivalent statement is to say the molecule has gone from a singlet state to a triplet state. After intersystem crossing, Stoke's losses can occur, and the molecule rapidly reaches the lowest vibrational level of the first excited triplet state. Depopulation of the triplet state can occur either by emission of a photon or a radiationless transition. In going from the triplet to the singlet, the spin changes from 1 to 0, which makes it a spin forbidden transition. For this reason, the lifetime of the triplet state is in the order of seconds. The T_1 to S_0 radiative transition is called phosphorescence.

Environmental Effects

Placing a benzene molecule in a solvent shifts the spectrum to the red relative to the gaseous state. This is true for the absorption, fluorescence, and phosphorescence. Two different shifts can occur if the solvent has two crystal forms. Cyclohexane is an example of this. It undergoes a solid-solid phase change at 186°K. Both phases cause a shift to the red, with the phase below 186°K causing the larger shift. There is disagreement at present about the crystalline form of cyclohexane; some recent work[12] suggests that there may be three crystalline phases of cyclohexane. The third is that obtained by freezing rapidly. This evidence is not conclusive, and since all the work referred to in this thesis can be explained by two phases, the one above 186°K and the one below, the phases will be called H and L. It is fairly certain that the phase above 186°K is cubic[10,11,12], and it has been suggested that the phase below 186°K is monoclinic[13].

Relative Intensity and Lifetime Measurements

Freezing the sample slowly allows the phase change to take place, in which case the cyclohexane is in phase L. In this case, a single spectrum is present. If the sample is frozen rapidly, some of phase H is retained, and due to the two environments the spectrum becomes doubled. The relative amount of the two crystal forms present depends on the freezing rate of the sample. At extremely fast freezing rates, primarily phase H is present.

An attempt has been made to measure the relative amount of absorption by the two lattices as a function of freezing rate.

The ratio of the intensities of the emission from phases H and L has also been measured. The relative intensity for the absorption does not always agree with that for the emission. The general nature of the result is that the fraction of phase H absorption is larger than the fraction of emission from phase H. This is especially true in the phosphorescence. Several possibilities exist as an explanation for this result. First energy transfer could be taking place from phase H to phase L. Phase L would then serve as an energy trap. Second, radiationless processes might depopulate the benzene excited states in phase H more than phase L. Third, the environment may effect radiative transition probabilities differently in the two phases.

Plate I shows the important processes just discussed and assigns rate constants to the different processes. It depicts energy levels for two benzene molecules, one of which is in phase H and the other in phase L.

For cases where the concentration is very low, the energy transfer from one phase to the other is negligible and one need only consider each molecule and its own processes. A derivation of a formula relating the relative intensities of the absorption and fluorescence follows. The result involves the rate constants defined in Plate I.

Let N_H and N_L be the steady state populations of the S_1 state for molecules in phase H and L, respectively. Steady state implies the number of molecules entering a state per unit time is equal to the number leaving per unit time. The number entering will be equal to the integrated intensity of the absorption. Intensity will be defined to be the number of transitions per unit time. The integrated intensity is the total number of absorption

EXPLANATION OF PLATE I

A diagram of the energy levels and rate constants for benzene in the two phases of cyclohexane. The rate constants are defined as follows:

k_{FH} = rate constant for fluorescence for benzene in phase H

k_{FL} = rate constant for fluorescence for benzene in phase L

k_{RSH} = rate constant for radiationless singlet transitions for benzene in phase H

k_{RSL} = rate constant for radiationless singlet transitions for benzene in phase L

k_{ISCH} = rate constant for intersystem crossing for benzene in phase H

k_{ISCL} = rate constant for intersystem crossing for benzene in phase L

k_{PH} = rate constant for phosphorescence for benzene in phase H

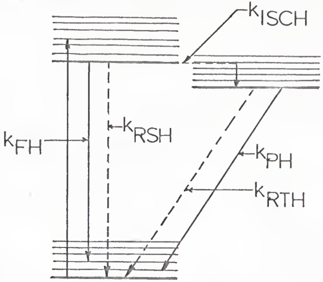
k_{PL} = rate constant for phosphorescence for benzene in phase L

k_{RTH} = rate constant for radiationless triplet transitions for benzene in phase H

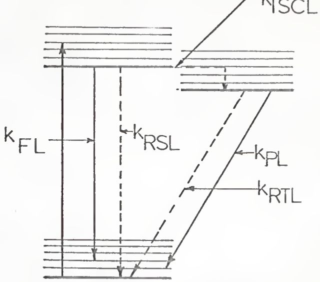
k_{RTL} = rate constant for radiationless triplet transitions for benzene in phase L

k_{TET} = rate constant for triplet energy transfer

PLATE I



PHASE H



PHASE L

transitions per unit time over the whole absorption band. The rate of absorption depends on the intensity of the exciting source. The source used had variations in intensity with wavelength. If a strong line were to coincide with a strong absorption peak, the rate of absorption would be large. This could result in populating the singlet state in one phase more than the other. However, the absorption bands are separated only 83 cm^{-1} in the S_0 to S_1 for phases H and L so that as long as the source does not vary drastically in that interval (83 cm^{-1} or approximately 6Å) the average of several absorption peaks should give a reasonable result. At equilibrium the rate of population of a state is equal to the rate of depopulation. The number of molecules per unit time leaving a state will be equal to the probability of leaving per unit time times the population of the state. The probability of leaving per unit time will be the sum of the various rate constants for leaving the state. The result is the

Intensity of absorption = (probability of leaving)(Number in state)

$$I_A = (k_F + k_{ISC} + k_{RS})N \qquad (1)$$

One can eliminate N by substituting $I_F = k_F N$ which yields

$$N = \frac{I_F}{k_F} \qquad (2)$$

Substituting (2) in (1) and solving for I_F gives

$$I_F = \frac{k_F}{k_F + k_{ISC} + k_{RS}} \quad I_A \qquad (3)$$

For two different phases, H and L, one thus has

$$I_{FH} = \frac{k_{FH}}{k_{FH} + k_{ISCH} + k_{RSH}} \quad I_{AH} \qquad (4)$$

and

$$I_{FL} = \frac{k_{FL}}{k_{FL} + k_{ISCL} + k_{RSL}} \quad I_{AL} \tag{5}$$

The ratio of the two equations is

$$\frac{I_{FH}}{I_{FL}} = \frac{k_{FL} + k_{ISCL} + k_{RSL}}{k_{FH} + k_{ISCH} + k_{RSH}} \; \frac{k_{FH}}{k_{FL}} \; \frac{I_{AH}}{K_{AL}} \tag{6}$$

The formula shows that the ratio of the fluorescence intensities is proportional to the ratio of the absorption intensities and that if one plots these two variables, the slope of the line is the coefficient on the right.

Since the intersystem crossing is the process by which phosphorescence takes place, and the intensity of the phosphorescence is comparable to the intensity of the fluorescence, the two rate constants, k_{ISC} and k_F, must have approximately the same magnitude. Several things suggest that k_{RS} might be small compared to k_F. The radiationless transitions for the triplet state have rate constants in the order of 10^{+1}-10^{-2}sec^{-1}, while k_F is in the order of 10^{+6}-10^{+8}sec^{-1}, and the energy difference between the first singlet and the ground state is larger than that between the first triplet state and the ground state. Windsor[14] comments that varying the environment does not greatly effect the lifetime of the singlet state. If $k_{RS} \ll k_F$, equation (6) reduces to

$$\frac{I_{FH}}{I_{FL}} = \frac{k_{FL} + k_{ISCL}}{k_{FH} + k_{ISCH}} \; \frac{k_{FH}}{k_{FL}} \; \frac{I_{AH}}{I_{AL}} \tag{7}$$

A similar expression can be obtained for the ratio of the phosphorescence intensities as a function of the fluorescence intensities by equating the rate of population of the triplet state to the rate of depopulation of the triplet state. The rate of population of the triplet state = $k_{ISC}N$, and the rate of depopulation of the triplet state = $(k_P + k_{RT})N'$, where N' is the population of the triplet state. Equating the two rates yields

$$k_{ISC}N = (k_P + k_{RT})N' \tag{8}$$

Using the intensity relationships

$$I_F = k_F N \quad \text{and} \quad I_P = k_P N', \tag{9}$$

solving for N and N', and then substituting into equation (8), one obtains

$$\frac{k_{ISC} I_F}{k_F} = \frac{(k_P + k_{RT}) I_P}{k_P} \tag{10}$$

Solving for I_P, one obtains

$$I_P = \frac{k_{ISC} k_P}{k_F (k_P + k_{RT})} \quad I_F \tag{11}$$

Labeling then the rate constants and the intensities for phases H and L, two equations result, and their ratio is

$$\frac{I_{PH}}{I_{PL}} = \frac{k_{PH}}{k_{PL}} \; \frac{k_{FL}}{k_{FH}} \; \frac{k_{ISCH}}{k_{ISCL}} \; \frac{(k_{PL} + k_{RTL})}{(k_{PH} + k_{RTH})} \; \frac{I_{FH}}{I_{FL}} \tag{12}$$

Thus, if one plots I_{PH}/I_{PL} versus I_{FH}/I_{FL}, one should obtain a straight line whose slope is the coefficient in the above equation. There is one more thing that can be done to simplify the above equation. The lifetime of the phosphorescence is determined by the total rate constant for depopulation of the triplet state, which will be $k_P + k_{RT}$. The lifetime is the reciprocal of the rate of depopulation, so for the lifetimes of the two states one has

$$\Upsilon_H = \frac{1}{k_{PH} + k_{RTH}} \tag{13}$$

and

$$\Upsilon_L = \frac{1}{(k_{PL} + k_{RTL})} \tag{14}$$

Substituting (13) and (14) into (12) one obtains

$$\frac{I_{PH}}{I_{PL}} = \frac{k_{PH}}{k_{PL}} \frac{k_{FL}}{k_{FH}} \frac{\tau_H}{\tau_L} \frac{k_{ISCH}}{k_{ISCL}} \frac{I_{FH}}{I_{FL}} \qquad (15)$$

From the measurements of relative intensity as a function of freezing rate, various values of the ratios of the intensities can be found and the data plotted. From the slope of the graph, the coefficient in equation (15) can be evaluated. The lifetimes for the two phases have been determined, so they can be substituted into the expression for the slope. This still leaves three ratios to be determined. Two of these can be evaluated from the absorption and fluorescence data, leaving just one ratio, which is determined by measuring the slope. This will be shown in the discussion of the results.

For high concentrations (above 1 per cent), one needs to consider the process of energy transfer from one phase to the other. A model for energy transfer from the H to the L lattice is as follows. Assume there are two adjoining regions in the crystal; in region H the crystal has the H lattice structure and in region L the L lattice structure. Assume that a benzene molecule in region H absorbs a photon. A few molecules away will be another benzene molecule. By some type of interaction, the energy is transferred from benzene molecule to benzene molecule in region H until it comes to a benzene molecule adjacent to region L. There will be a slight energy difference between triplet states of benzene in molecules in region H and those in region L, with those in region L having the lower energy. Because the energies are so nearly the same, there is a good chance for transfer of energy to the benzene molecule in region L, the excess energy being given to the lattice. Thus, region L serves as a trap for the energy and increased phosphorescent emission from the L lattice occurs. The singlet energy transfer should be much smaller than the triplet because the lifetime of the state is approximately 10^6 times as long.

Robinson et al.[31] suggest that the process of energy transfer is one in which host molecules participate as well as guest molecules. In this case, then, the interaction involves the cyclohexane. The wavefunction of a benzene molecule in a crystal lattice cannot be entirely separated from the total wavefunction of the crystal. An interaction energy of 12 cm^{-1} is suggested by Robinson as a rough universal value. From a theoretical analysis, Robinson derives a formula for the dependence of the energy transfer on concentration. He shows that, for an excited triplet state with a lifetime of 1 sec and an energy difference of 12,000 cm^{-1} between the lowest excited state of the guest and the lowest excited state of the host, energy transfer between 4 intermediate molecules should be efficient. This result is derived for the case where the temperature of the sample is 0°K. At higher temperatures, transfer should become more efficient.[31] An average of four intermediate molecules would correspond to a concentration of about 1 per cent.

This will have an effect on the lifetime of the triplet state for the two phases. For the phase H this will provide another path for depopulating the state so the lifetime will be shorter:

$$\tau_H = \frac{1}{k_{PH} + k_{RTH} + k_{TET}} \qquad (16)$$

For phase L, this provides another way of populating the triplet state. When the exciting light is cut off, the triplet energy transfer does not stop immediately and as a result the lifetime of the phosphorescence is somewhat different. The equations for this process are worked out in the appendix. Due to the difficulty of obtaining the rate constant for triplet-triplet energy transfer as a function of concentration and freezing rate, one should look at the case where the triplet energy transfer constant is large compared to the rate of phosphorescence for the phase H. In this case, the rate of transfer out of the triplet state for the H phase is large so the population of the triplet state is small, and the phosphorescent emission intensity is low. The energy is with high probability transferred to the other phase. When the exciting light is cut off, the energy transfer stops rapidly because the population of the triplet state for phase H is small and the rate of depopulation is large. Therefore, in measuring the lifetime of the phosphorescence for phase L, the result is the same as if only one phase were present. By examining some of Hirayama's work where he measured lifetime as a function of concentration, one can see this effect, as will be explained below. Also, the intensity of the phosphorescence from phase H is very low for high concentrations, which also agrees with the theory of such a process.

EXPERIMENTAL PROCEDURES

Spectrograms and Lifetimes

The block diagram shown in Fig. 3 indicates the general nature of the set up used to obtain the spectrograms and the intensity decay curves for lifetime measurements. Plate II shows a photograph of the equipment that was normally used. The source used was a GE-H6 high pressure (approximately 120 atm) mercury lamp. This lamp has a quartz jacket and is rated at 1000 watts input: it is a good source of ultraviolet radiation. The power supply for the lamp was built using a variac and several surplus transformers. The lamp normally operates at 850 volts and 1.4 amps a.c. A starting voltage

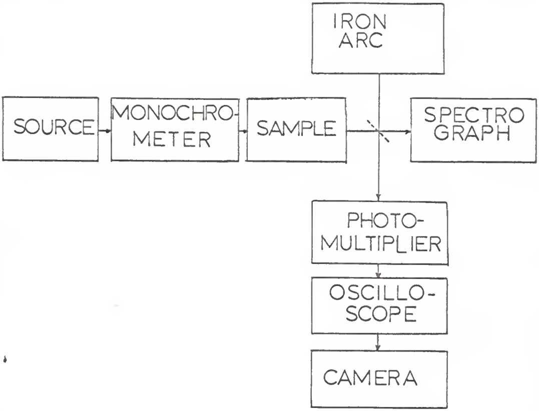


Fig. 3

of approximately 1200 volts is needed. A schematic diagram of the circuit used is shown in Fig. 4. The inductance limits the current to about 3.5 amps during the starting period when the B-H6 has a low resistance.

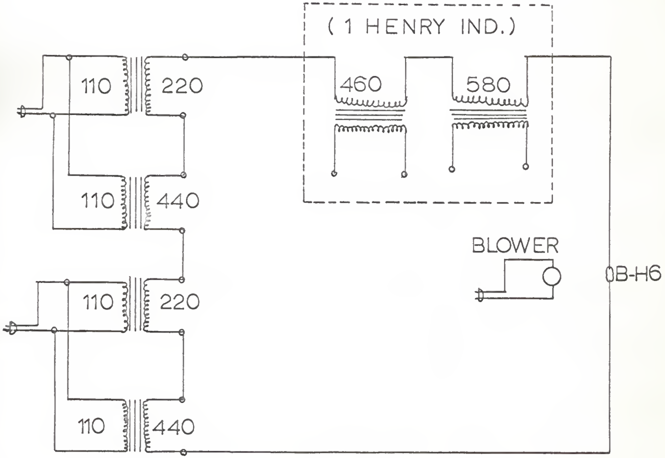


Fig. 4 POWER SUPPLY

The specifications call for an air compressor to cool the lamp. However, satisfactory results were obtained using a General Electric 7500 rpm 1/4 horsepower blower which is called an ELECTRON TUBE COOLER, Model A, Type CS45-404 and is made by ROTON DIVISION, 180-220 Weeden Street, Pawtucket, Rhode Island. The arrangement of the cooler and lamp is shown in Plate III.

Due to the high pressure, the mercury lines are broadened considerably, and one gets roughly a continuous emission from the lamp. The 2537Å line, which is usually strong in the mercury spectrum of low pressure lamps, is missing because of self absorption.

A Bausch and Lomb quartz monochrometer was used to limit the exciting light to those wavelengths which the samples absorbed. By adjusting the entrance and exit slits, the band pass could be selected as desired. The slit widths on the monochrometer were usually set at 2 mm, which gave a bandpass from approximately 2300Å to 2650Å.

To focus the light emerging from the monochrometer on the sample, a quartz lens and a front surface mirror were used. Plate IV shows a diagram of the optics and Plate V a picture. An image of the monochrometer slit was focused on the bottom of the sample holder by lens No. 1. The emission from the sample was reflected from mirror No. 2 and an image of the sample was focused on the spectrograph slit by lens No. 2. A solution of 240 g/liter of $NiSO_4$ and 45 g/liter of $CuSO_4$ was used as a filter[15] to remove unwanted scattered light coming through the monochrometer. The filter absorbs nearly everything longer than 3000Å.

To observe emission of long lifetime, a Becquerel type phosphoroscope[16] was sometimes used. However, in most experiments the total emission of the sample was recorded.

Plate VI shows a picture of a sample cell. The cell has a quartz window at the top. This cell is basically that described by Heckman[17] and by Kanda and Sponer[18]. The quartz window is sealed to the pyrex cell with "Torr-Seal" produced by Varian Associates, Vacuum Products Division, Palo Alto, California. The cell is approximately 35 cm long and 3.5 cm in diameter. Tungsten wires were passed through the wall of the cell to make electrical connection to a thermocouple at the bottom of the cell.

[illegible] iron arc operated at 220 volts and [illegible] amps D. C. was used to put a comparison spectrum beside the benzene spectrum.

The spectrograph is a Bausch and Lomb medium quartz prism spectrograph. It was focused and the slit aligned to give vertical lines on the plate. The slit widths commonly used were 50 μ for the benzene emission and 10 μ for the iron arc.

Two types of plates were used in taking the spectra. For the wavelength region from 2300Å-5000Å, Kodak 103a-O plates were used; for the region from 5000Å-7000Å, 103a-F plates were used. These plates are particularly sensitive to light of low intensity. Most of the plates were taken on 103a-O plates because of interest in the 2300Å-2600Å absorption of benzene. The plates were developed using Kodak D-19 developer, stop bath, and rapid fixer. The development time was always kept at four minutes because relative intensity measurements were wanted. The stop bath was used to definitely stop the development time at four minutes. The exposure time was generally three hours. These two factors were kept constant to keep the contrast constant from plate to plate.

Using these specifications for exposure and development, a set of seven exposures of the source was taken on the same plate. These exposures were taken to determine the relation between relative intensity and densitometer deflection. The emission from the T-[illegible] was reflected from a white card to reduce its intensity. Then a lens focused the light on the spectrograph. A diaphragm was placed as close to the lens as possible so that the intensity was proportional to the area of the opening in the diaphragm. Seven openings of the diaphragm were used, and a three hour exposure taken with each. Densitometer tracings were made of each exposure, and scale of relative intensity versus deflection was devised. The γ value for the contrast agreed with Kodak's value. Due to the number of variables present[19a], the relative intensity measurements have more uncertainty than those taken using photoelectric devices.

Measurement of Wavelength and Frequency

All the wavelength measurements were made by comparing the unknown with the iron spectrum. The values for the wavelengths of the iron lines were taken from Brode's book[20], which has an enlargement of the iron spectrum, and the MIT wavelength tables[21]. The wavelength's were converted to wavenumbers using the Cauchy formula[22] for the index of refraction of air. This conversion was done on the computer for all the iron lines labeled in Brode's spectral maps. Enlargements of the iron spectrum were made and approximately 1,000 lines were labeled.

Two methods were then used to make measurements on the unknowns. One method involved making enlarged prints of the spectra with a magnification of about 20x from the plates. The enlargements show both the iron and the unknown spectrum, side by side. Then either by linear interpolation, which is quite time consuming for a plate with over 100 lines, or the Hartmann dispersion formula[23] the wavelengths and frequencies can be computed. The second method involved making densitometer tracings that are approximately 50 feet in length. The iron spectrum was traced and then labeled in wavenumbers (approximately 10 cm^{-1}/inch). The unknown spectrum trace was made by tracing from the plate near the border between the unknown and the iron comparison spectrum. When there was a space with no unknown lines, the rack would be shifted slightly to pick up iron lines. This gave calibration points about every two to three feet on the tracing. The unknown tracing was then laid over the iron tracing and the values could be read immediately. The iron lines on the known and unknown would generally match within 2-3 cm^{-1}. This has the advantage of being much faster (approximately two hours to measure the fluorescence), but the disadvantage that the weak lines do not show too well.

The best procedure, as far as accuracy, completeness, and format are concerned, is to use the Hartmann dispersion formula and take the distance measurements from the enlargements. The distance measurements are then fed into the computer, which is programmed to compute the constants in the Hartmann formula and the wavelengths of the unknown spectrum, convert the wavelengths to wavenumbers, and print out the results. Six known iron lines are measured as unknowns and their values computed as a check on the accuracy of the dispersion formula and measurements. The computer program is in the appendix.

Lifetime Measurements

Because the lifetimes of triplet states in organic solids are the order of 10^{-1}-10^{+2} seconds, it is relatively easy to measure the lifetimes of these states. A 1P28 photomultiplier tube with a 1000 volt D. C. power supply was used. A 1 megohm resistor was connected from the anode to ground, and the voltage drop across the resistor was fed directly into a Tektronix 545 oscilloscope. A Tektronic C-12 oscilloscope camera with a polaroid back was used to photograph the trace.

Samples

Most of the spectrograms taken were of mixed crystals of benzene in cyclohexane. To reduce the broadening of the spectral lines and the probability of radiationless transitions to the ground state, the samples were cooled to liquid nitrogen temperatures.

The first plates were taken with Eastman's spectrograde benzene and cyclohexane. The plates showed a background at wavelengths a little longer than the phosphorescence of benzene. The intensity decays were non-exponential. It was suspected that there was an impurity in the cyclohexane, so a sample was prepared with "pure" cyclohexane. The sample did phosphoresce weakly at longer wavelengths: the excitation spectra had a single rather sharp peak at 2850Å. The emission did not exactly coincide with the background in the spectrum with benzene present, but was similar. The lifetime of the cyclohexane emission was measured and found to be 1.4 sec. Cyclohexane was then purchased from Matheson, Coleman, and Bell Company. No emission was observed from this cyclohexane when the sample was exposed to UV radiation. It was possible to remove the impurity from the Eastman cyclohexane by a method suggested by Dana Johnson[24].

Using the new cyclohexane did not entirely eliminate the background in the benzene spectra. Also, the intensity decay of the samples still did not give exponential decay curves. The background in the phosphorescent region was concentration dependent. The background was absent for low concentration samples and strong for high concentration samples. Before the optics were covered, scattered light resulted in a background. This can be seen on Plate XIII for the 69°/min trace. In preparing a fresh sample one time in which the sample bottle had not been washed with cleaning solution (saturated solution of K_2CrO_4 in concentrated H_2SO_4), it was discovered that the decay curve was exponential. At the same time there was a significant decrease in the visible phosphorescence from the sample in the 4000Å region. From further experimenting, it was verified that the cleaning solution affected the spectrum and lifetime. To check this a fresh sample was prepared using a sample bottle that had been rinsed with KOH. Also a sample of 1 per cent concentration was prepared with a sample bottle that had been washed with cleaning solution and rinsed once with distilled water. The sample was allowed to stand overnight and then the spectrum and lifetime were taken. One could see there was definitely more phosphorescence from the sample that had been in the bottle washed with cleaning solution. Also, the spectrum gave a background in the phosphorescence and a non-exponential decay. The other sample showed no background and give an exponential decay. It was also apparent that the samples that stood in the sample bottles longest gave the most background in the spectrum. These backgrounds were unstructured, so there is little danger that the measured spectral lines are impurity lines. Plate XI shows a 1 per cent and a 10 per cent benzene in cyclohexane slow frozen spectrum. The 1 per cent sample was fresh and prepared in a sample cell rinsed in KOH, while the 10 per cent sample was stored for approximately six months in a sample bottle that had been rinsed with cleaning solution. One can see the large background in the phosphorescence for the 10 per cent sample. The effect of the small amount of cleaning solution can be more easily understood if one realizes that a 1 per cent sample would have approximately .02 ml of benzene in the sample cell and the .01 per cent sample would have only .0002 ml of benzene in a cell with 2 ml of cyclohexane.

Using fresh samples and sample cells that had not been rinsed with cleaning solution, exponential decay curves were obtained for the various concentrations with slow freezing.

Preparation of the Sample

To prepare the mixed crystals, benzene and cyclohexane were cooled with liquid nitrogen. The freezing points of benzene and cyclohexane are respectively 4°C and 6.5°C, but they form a eutectic mixture. Upon cooling, cyclohexane undergoes a solid-solid phase change at 186°K. Spangler and Sponer[2] observed that the transition from phase H to phase L was only partially complete if the sample was frozen rapidly. To study this process in more detail, a method of controlled cooling was devised. Temperature control of the sample was achieved by use of liquid nitrogen as a heat sink and heating coils, as shown by Plate VII. By varying the heater current the temperature of the sample was varied. A variac was connected to the heating coil and by a driving mechanism the variac voltage was gradually reduced to zero. By varying the driving rate the cooling rate could be varied. A thermocouple was used to monitor the sample temperature. The thermocouple was placed inside the sample cell and buried just beneath the surface of the sample. This is also shown in Plate VII. The thermocouple was made of fine copper-constantan wires to minimize heat conduction. To maintain the junction and the sample at a uniform temperature, a copper disc was soldered to the junction buried in the sample. Ice water was used to provide a reference temperature and a John Fluke Model 803B AC/DC differential voltmeter was used to measure the EMF developed by the thermocouple. The thermocouple calibration data was taken from the AIP Handbook.[25]

As can be seen from Plate VIII, the cooling curves are nearly linear in the region of interest except for the inflection point at 186°K where the phase is changing. The cooling rate while passing through the phase transition is zero, though heat is still being removed from the sample.

[illegible], [illegible] cooling rates between [illegible].

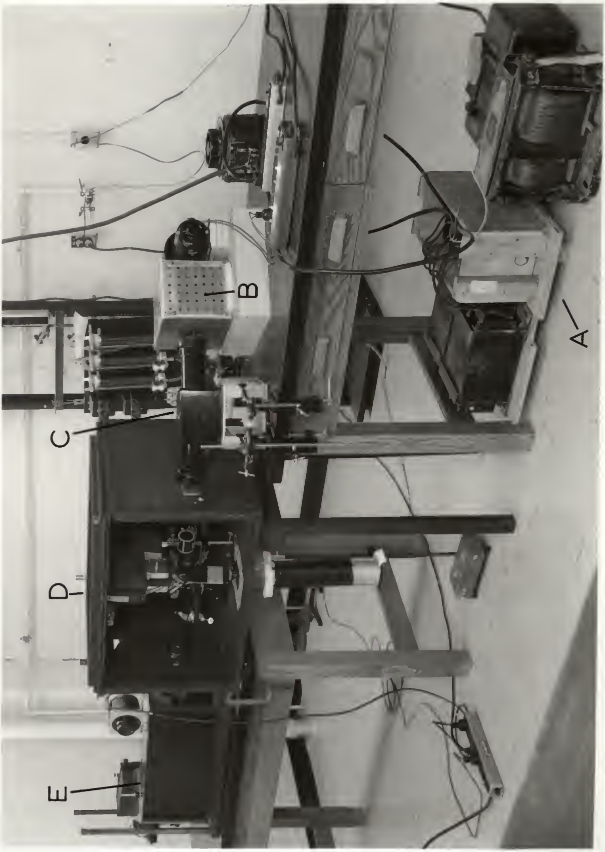
The freezing of the samples was carried out by pipetting 2-3 ml of benzene-cyclohexane solution into the sample cell. The sample cell was then connected to the vacuum system and the sample frozen rapidly by immersing it in liquid nitrogen. When the sample had frozen, the cell was evacuated, and then the sample was allowed to melt. This was done to remove any dissolved gases from the sample. After melting, the sample was frozen using the apparatus described above. For a faster freezing rate, samples were frozen by just immersing the evacuated sample cell directly in liquid nitrogen. This way freezing rates up to 200 degrees per minute were attainable. To get fast cooling rates, very thin samples must be used so that the cooling will be uniform. A number of experiments were performed where the samples did not make good physical contact with the sample cell and thermocouple so that the thermocouple did not show the actual freezing rate.

EXPLANATION OF PLATE II

A picture of the source, monochrometer, optics, and spectrograph.

A. Power Supply
B. Light Source
C. Monochrometer
D. Optics
E. Spectrograph

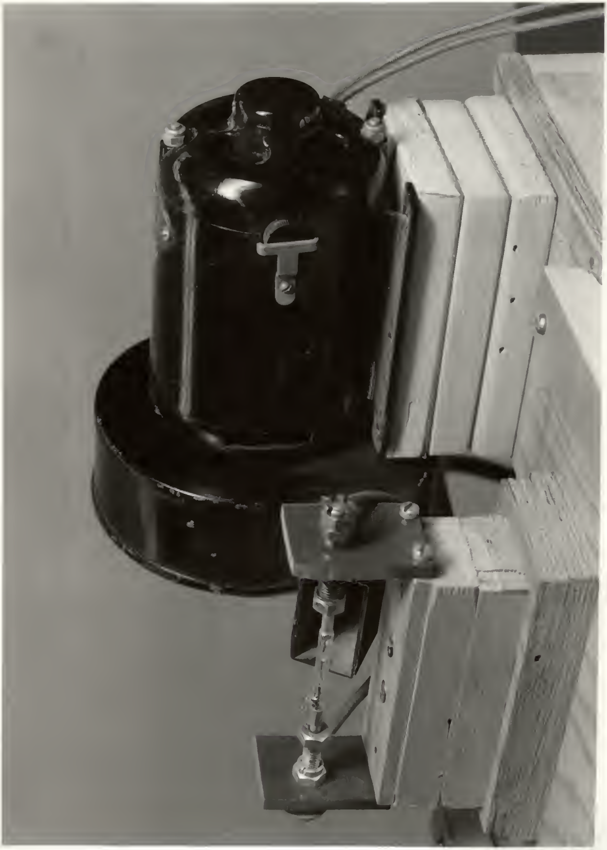
PLATE II



EXPLANATION OF PLATE III

A picture of the B-H6 mercury high-pressure lamp and cooling fan.

PLATE III



EXPLANATION OF PLATE IV

A diagram of the optical set up, photomultiplier, and sample cell.

A. Lens 1

B. Filter

C. Mirror 1

D. Sample Cell

E. Mirror 2

F. Lens 2

G. Photomultiplier

H. Sample

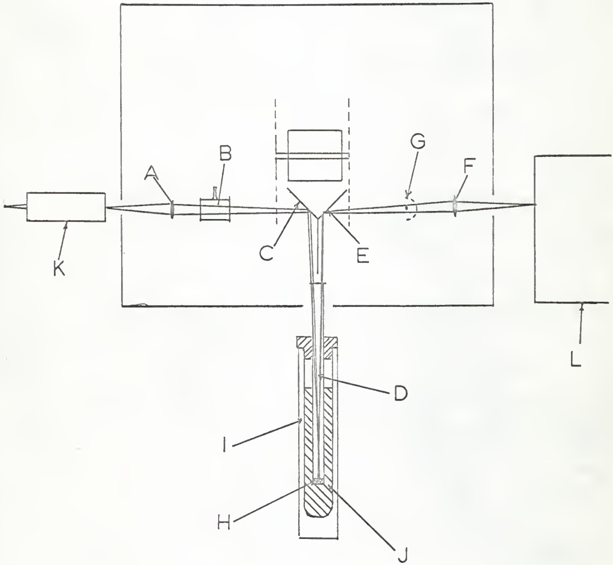
I. Dewar

J. Liquid Nitrogen

K. Monochrometer

L. Spectrograph

PLATE IV



EXPLANATION OF PLATE V

A picture of the optical set up, photomultiplier and sample cell.

A. Lens 1

B. Filter

C. Mirror 1

D. Sample Cell

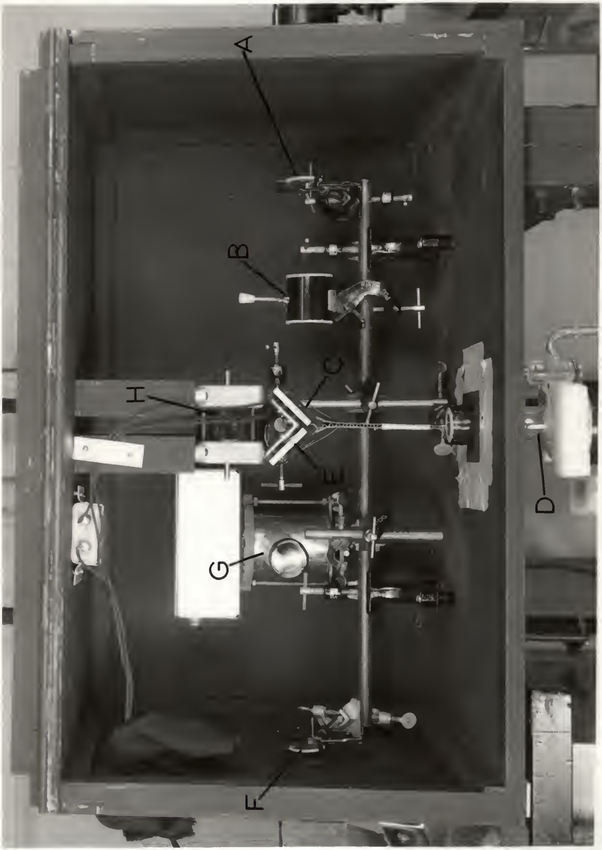
E. Mirror 2

F. Lens 2

G. Photomultiplier

H. Motor to Drive Phosphorescope Discs

PLATE V



EXPLANATION OF PLATE VI

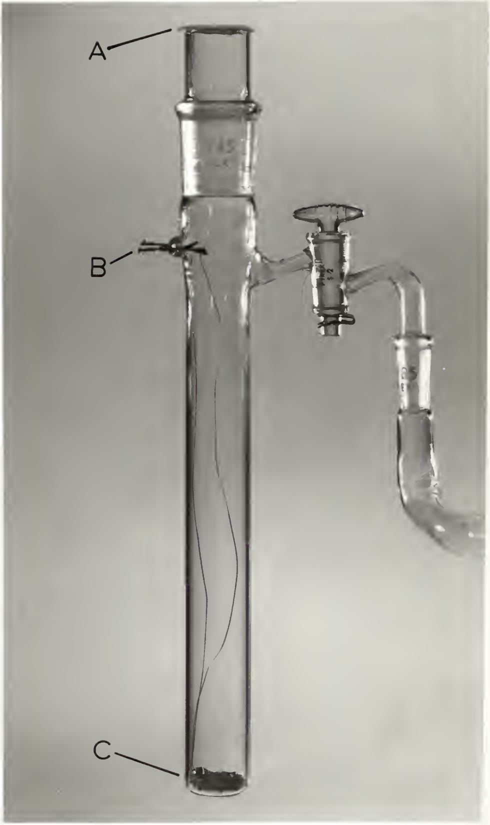
A picture of the sample cell.

A. Quartz window

B. Tungsten wires

C. Thermocouple

PLATE VI



EXPLANATION OF PLATE VIII

A picture of the equipment used to cool the samples.

A. Sample Cell

B. Heater

C. Heater Power Supply

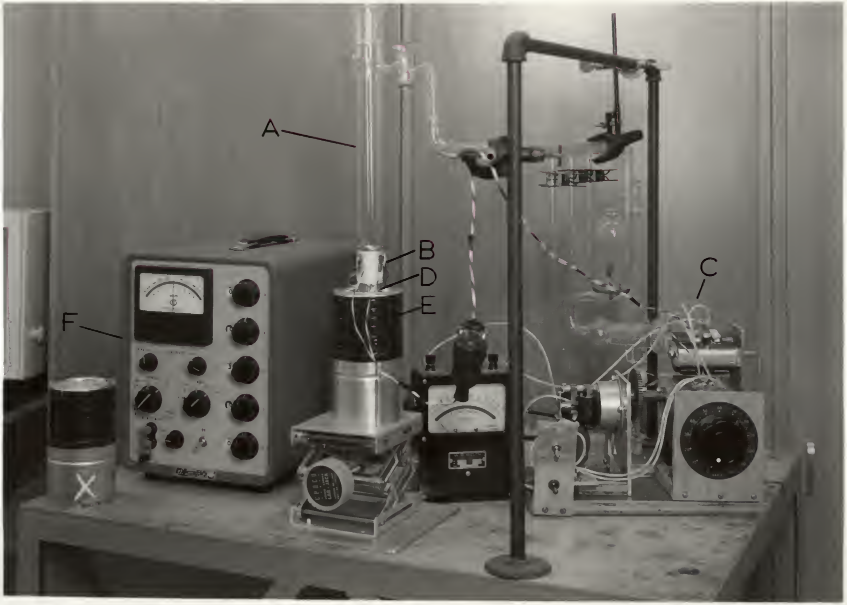
D. Copper Foot

E. Liquid Nitrogen Bath

F. Null Voltmeter

G. Ice Water Reference

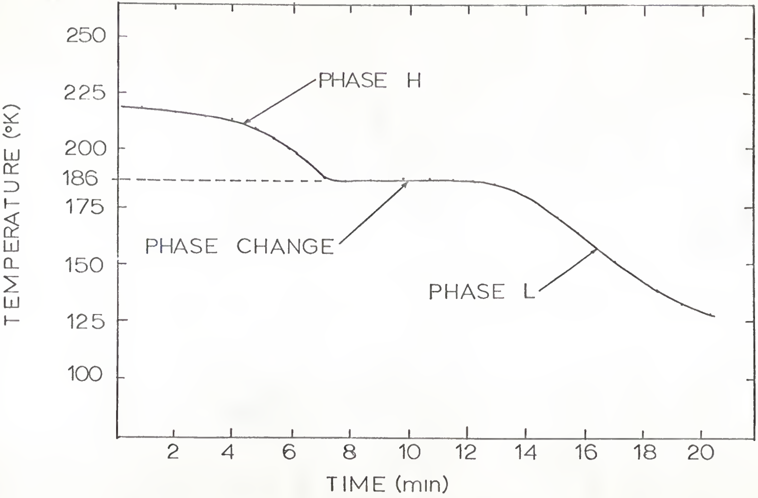
PLATE VII



EXPLANATION OF PLATE VIII

A graph of a cooling curve for a benzene-cyclohexane solution showing the solid-solid phase transition and the two phases of cyclohexane.

PLATE VIII


TEMPERATURE (°K)
250
225
200
186
175
150
125
100
TIME (min)
2
4
6
8
10
12
14
16
18
20
PHASE H
PHASE CHANGE
PHASE L

RESULTS

Relative Intensity Studies

A densitometer trace of the spectrum of a slowly frozen sample of benzene in cyclohexane is shown in Plate IX. It was possible to see some of the absorption spectrum (actually selective reflection) because part of the incident exciting light was diffusely reflected off the surface of the sample. By using a monochrometer, the exciting light was limited to the region of benzene absorption. The ability to monitor all three regions simultaneously allowed observation of differences in relative intensities of absorption and emission by benzene molecules in the two different crystal forms of cyclohexane (vide infra).

By taking the spectrum of benzene in the cyclohexane crystal lattice at various temperatures, one can note the shift in frequency related to the two crystal forms. Plate X shows densitometer tracings of the spectrum at various temperatures. There are several things to note from these tracings. First, as the temperature rises above 186°K the absorption and fluorescence bands shift to the blue by approximately 80 cm^{-1}; this shift correlates with the phase change in the cyclohexane crystal. A shift of a few wavenumbers occurs upon raising the temperature from 77°K to 170°K. Second, as the temperature increases the bands become broader. The half width is nearly equal to kT, where k is Boltzman's constant and T is the temperature of the sample. Third, the phosphorescence is absent at the higher temperatures due to the greatly increased probability of competing radiationless transitions.

Plate XI shows the spectra for slowly frozen samples of various concentrations. The 5 per cent and 10 per cent samples show spectral lines in absorption and fluorescence that are present in the spectrum of pure crystalline benzene and also show a continuous background in the phosphorescence and in the fluorescence. The former effect has been observed previously in absorption by Spangler and Sponer[2] and was attributed to the segregation of microcrystals of benzene during the freezing of higher concentration solutions. The latter effect is discussed below.

When the samples are frozen rapidly, the bands become doubled. Plate XII shows this effect on a .1 per cent sample. With rapid freezing a spectrum essentially identical to that obtained with slow freezing but shifted 83 cm^{-1} to the blue in absorption and fluorescence and 59 cm^{-1} to the blue in phosphorescence appears. This effect has been noted by Coupron, et al.[30] and studied by Spangler and Sponer[2]. Correlating this shifted spectrum with that shown in Plate X for the two crystal forms, they concluded that the doubling was a result of having the two crystal forms present at 77°K. The 83 cm^{-1} shift is the same in fluorescence and in the absorption. This is expected because the same electronic transition is involved in the two processes.

By observing all three regions of the spectrum simultaneously one was able to detect a concentration dependent effect that had not previously been observed. Plate XIII shows spectra of samples of various concentrations, all fast frozen to give two peaks. The thing to be noticed is that in the fluorescence and phosphorescence regions the relative intensities of the emission from phase H and phase L do not agree with the relative intensity in the absorption spectrum. The trace of the .01 per cent sample shows the absorption and fluorescence have nearly the same relative intensities. The trace of the .1 per cent sample shows absorption characteristic of phase H and fluorescence predominately, but not wholly, phase H. In the phosphorescence, however, the emission is equally intense from the two crystal forms. For the 1 per cent sample, the absorption is characteristic of the cubic lattice, but fluorescence is stronger from phase L. The phosphorescence for the 1 per cent sample is also stronger from phase L, and the shift in relative intensity is even more pronounced. For the 5 per cent sample, almost all the absorption is related to phase H and some segregated benzene microcrystals, yet the fluorescence shows the greater emission from the phase L lattice. The phosphorescence is from the phase L lattice. In summary, one can see that the concentration has a large effect on the crystal form from which the emission originates. A mechanism of energy transfer from one crystal form to the other was suggested in the chapter on theory.

The relative intensities of the two peaks in the absorption spectrum can be taken as an indication of the relative amounts of the two crystal forms present. From the relative intensity measurements, a graph of the percentage of phase H (cubic) absorption versus the freezing rate can be plotted: this is shown in Plate XIV. Points for all the concentrations involved are fit by the same curve. From this figure, one can see that the relative amounts of the two lattice forms present are not strongly concentration dependent. This indicates that freezing rate alone determines the amounts of the two crystal forms that are present. The slow frozen high concentrations deviate because benzene segregates out and forms microcrystals. These microcrystals absorb at nearly the same place as phase H.

It has already been pointed out that the relative intensities in the emission and absorption do not agree. This result seems to indicate that, at concentrations above 1 per cent, energy that is absorbed by benzene molecules in the cyclohexane phase H is with high probability radiationlessly transferred to benzene molecules located in a region where the cyclohexane crystal form is phase L. For low concentrations the ratio of the absorption intensities should be proportional to the ratio of the fluorescence intensities. Plate XV shows a graph of the data for a .1 per cent sample. A straight line fits the data and the slope is 1.03 ± .27. Also, a graph of the ratio of the phosphorescent intensities for phase H and phase L was plotted versus the ratio of the fluorescence intensities. The result can also be fitted with a straight line whose slope is .43 ± .09.

Lifetime Measurements

Plates XVII and XVIII show pictures of the decay curves and the plots of the ln(intensity) versus time for slow frozen samples. These pictures represent the intensity decays after the impurities had been removed. All the points fall well within their uncertainties and the logarithmic plots result in straight lines. Table 1 shows the lifetime and their probable errors.

Table 1

Lifetime of Benzene in Cyclohexane for Various Concentrations

Lifetime (sec)	Concentration (per cent)
4.6 ± .2	.01
4.6 ± .1	.1
4.35 ± .04	1
4.25 ± .04	5
4.0 ± .2	10

Plate XIX summarizes the results; the points for the various concentrations are the average of several experiments.

It was difficult to obtain the lifetime of the emission from phase H. For concentrations below .1 per cent, the intensity was too low to get good traces, and for concentrations higher than .1 per cent, the emission came primarily from the L phase. The problem is compounded because the phosphorescent emission is only 1/2 as strong from phase H as from phase L for an equal absorption intensity even without any energy transfer (see the 0.01 per cent trace on Plate XIII). Therefore, to measure the lifetime it was necessary to freeze the sample as rapidly as possible and then analyze the decay curve as the sum of two decay curves. This is shown in Plate XX. This was done three times, resulting in 1.0, 1.0 and 1.2 seconds for the lifetime of the benzene in phase H. From the analysis of the decay curve, one was able to predict within 10 per cent the relative intensities that the phosphorescence would show on the plate.

Measurements of Wavelengths

The wavelength measurements for a slow frozen sample are given in Table 2. The splitting observed in the fluorescence is 83 cm^{-1} between phase H and phase L. This is the same as was observed in the phase H absorption.

The strong bands in absorption show satellite bands in the absorption at one, two and three times 35 cm^{-1} displaced to the higher energy side. The fluorescence also shows satellite bands at approximately 40, 80 and 148 cm^{-1} to the lower energy side of the stronger bands. The satellite bands are seen quite clearly on the (0, 0) transition. They are more diffuse than the other bands which sets them apart from lines due to the vibration of the molecule.

From a number of plates the first fluorescence strong band was measured as 37, 107 cm^{-1} which implies the (0, 0) would be 37,714 cm^{-1}; Leach[3] gives 37,715 and Spangler and Sponer[2] give 37, 718 cm^{-1}. This is good agreement considering the half width of the bands is approximately 50 cm^{-1}.

Table 2. Measured frequencies for a .1 per cent slowly frozen sample.

Absorption: $0_L = 37{,}718$ cm^{-1}, $0_H = 37{,}802$ cm^{-1}

Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity
38,231	S	40,596	W
38,270	VWVD	40,656	W
38,318	WVD	40,712	VW
38,489	WD	40,734	VW
38,638	M	40,781	M
38,674	MW	40,809	VVW
38,743	WVD	40,868	VVW
38,859	M	40,897	W
38,882	VW	40,999	MS
39,565	VW	41,030	VVW
39,603	VW	41,073	VVW
39,672	WVD	41,106	VW
39,732	VW	41,231	VW
39,782	MW	41,259	W
39,810	MW	41,325	W
39,884	W	41,469	VVW
39,976	W	41,512	VW
40,080	S	41,575	W
40,120	VVWD	41,640	VWVD
40,150	VVW	41,700	WD
40,188	VW	41,823	VVW
40,492	VW	41,862	VVW
40,536	W	41,912	VVW

Fluorescence: $0_L = 37{,}718$ cm^{-1}

Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity
37,142	WHD	36,112	VS
37,108	VS	36,073	MWH
37,072	WHD	36,020	MW
37,035	VWHD	35,965	VVW
36,960	VVW	35,916	VW
36,911	VVW	35,881	VVW
36,726	W	35,783	MW
36,637	MW	35,755	VW
36,543	VW	35,734	W
36,310	VVW	35,704	MW
36,169	L	35,641	MW
36,129	S	35,552	W

Table 2. Continued

Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity
35,415	W	34,096	VW
35,178	M	34,042	W
35,144	MS	33,899	VVW
35,117	S	33,808	W
35,082	MW	33,781	VVW
35,030	MW	33,720	VW
34,975	VVW	33,678	WHD
34,923	VVW	33,664	WHD
34,889	VW	33,574	VVW
34,795	M	33,428	VW
34,763	VWVD	33,202	VWD
34,711	MW	33,175	VWD
34,673	WH	33,138	MW
34,657	MW	33,107	VVW
34,564	VW	33,057	VVW
34,504	VVWD	32,821	VW
34,422	W	32,790	VVW
34,188	M	32,736	VVW
34,160	M	32,686	VWD
34,130	S		

Phosphorescence: $0_L = 29,442$, $0_H = 29,501$

Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity
28,835	VVW	27,000	VVWD
28,735	W	26,903	WH
28,638	VW	26,870	S
28,449	M	26,844	MS
28,266	MS	26,770	VVWD
28,072	VVW	26,659	VVWD
27,989	VVW	26,615	VW
27,890	WH	26,574	VVW
27,855	S	26,476	WD
27,832	MH	26,291	M
27,748	VW	26,170	VW
27,644	VW	26,083	WVD
27,606	VW	26,013	VWVD
27,457	VW	25,919	W
27,419	VVW	25,388	S
27,277	MS	25,856	M
27,085	VVW	25,692	VWVD
27,051	VVW	25,593	VVW

Table 2. Continued

Wavenumber (cm^{-1})	Intensity	Wavenumber (cm^{-1})	Intensity
25,514	W	24,683	MW
25,477	VW	24,534	W
25,300	W	24,494	VVWD
25,268	VVW	24,318	VVW
25,229	VVW	24,210	VVW
25,184	VW	24,133	MW
25,111	MW	24,104	W
25,089	WH	23,928	VVW
24,954	VVWD	23,824	VVWD
24,905	M	23,736	VVW
24,874	W	23,694	VW
24,809	VVW	23,146	VVWD
24,710	W		

Intensity Abbreviations: V = Very, W = Weak, M = Medium, D = Diffuse, H = Shoulder, S = Strong

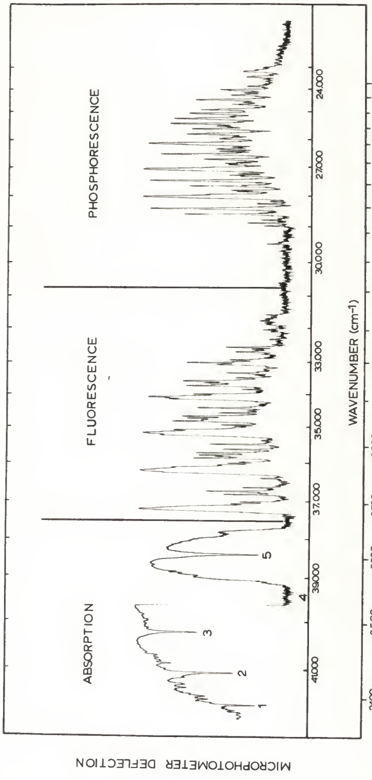
EXPLANATION OF PLATE IX

A densitometer tracing of a spectrum of slow frozen benzene in cyclohexane. The spectrum is of a 1 per cent sample.

1, 2, 3, 5 are strong absorption bands of benzene.

4 is a self-absorption in the source.

PLATE IX

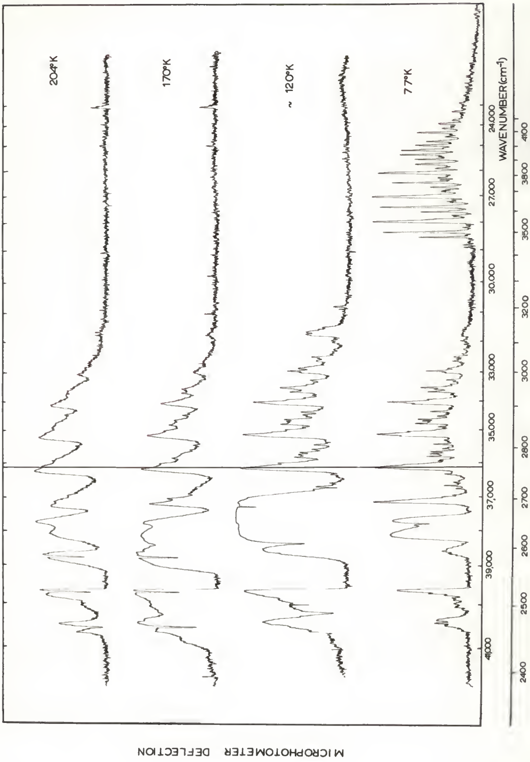

ABSORPTION
FLUORESCENCE
PHOSPHORESCENCE
1
2
3
4
5
41,000
39,000
37,000
35,000
33,000
30,000
27,000
24,000
WAVENUMBER (cm⁻¹)
2400
2500
2600
2700
2800
3000
3200
3500
3800
4100
WAVELENGTH (Å)
MICROPHOTOMETER DEFLECTION

EXPLANATION OF PLATE X

Densitometer tracings of the spectrum of a 1 per cent sample for four different temperatures. The tracings were taken starting at $77^{\circ}K$

The shift in the wavelength between $170\text{-}204^{\circ}$ corresponds with the change from phase L to phase H.

PLATE X


204°K
170°K
~ 120°K
77°K
24,000
27,000
30,000
33,000
35,000
37,000
39,000
41,000
WAVENUMBER(cm^{-1})
4100
3800
3500
3200
3000
2800
2700
2600
2500
2400
WAVELENGTH (Å)
MICROPHOTOMETER DEFLECTION

EXPLANATION OF PLATE XI

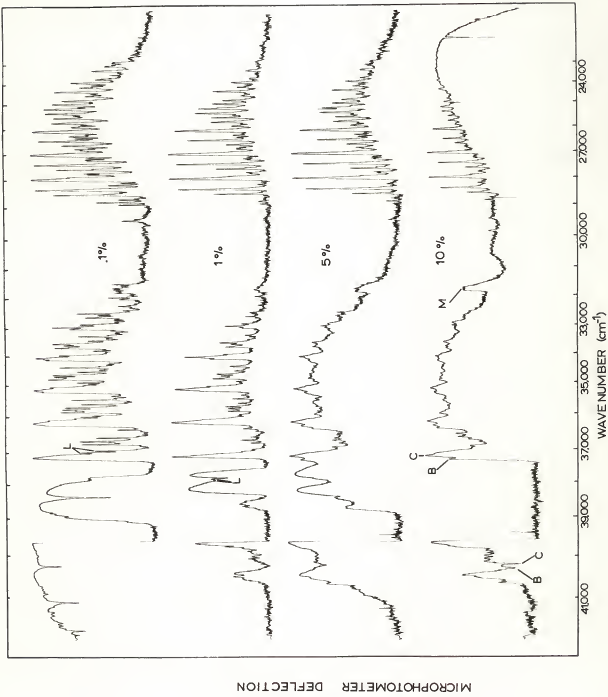
Densitometer tracings of the spectrum of benzene in cyclohexane for various concentrations taken at liquid nitrogen temperature. The 1 per cent sample was fresh and prepared in a sample cell that had been rinsed with base. The 10 per cent sample was prepared about 6 months before the spectrum was taken. It was stored in a sample bottle that had been soaked in cleaning solution.

B - benzene microcrystals

C - benzene in phase L

M - mercury

PLATE XI


.1%
1%
5%
10%
L
L
B
C
B
C
M
41,000
39,000
37,000
35,000
33,000
30,000
27,000
24,000
WAVE NUMBER (cm^{-1})
MICROPHOTOMETER DEFLECTION

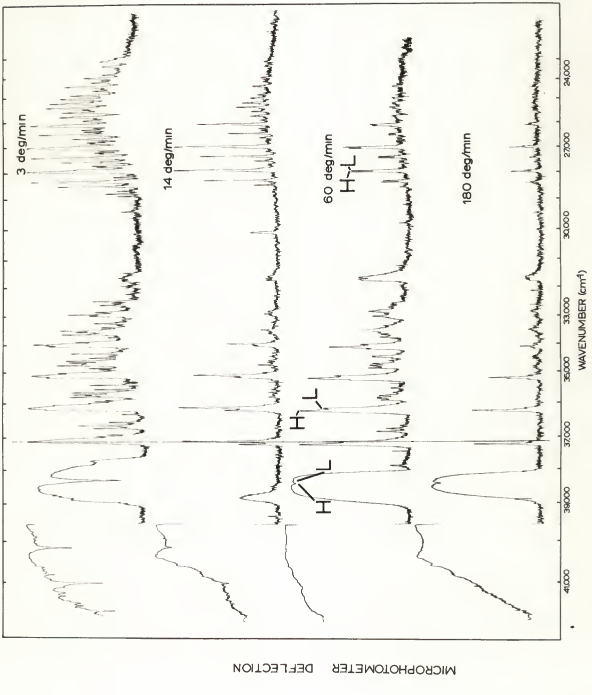
EXPLANATION OF PLATE XII

The plate is made up from densitometer tracings of the spectrum of .1 per cent samples frozen at different rates. The plate shows the two components related to the phases H and L.

H - phase H

L - phase L

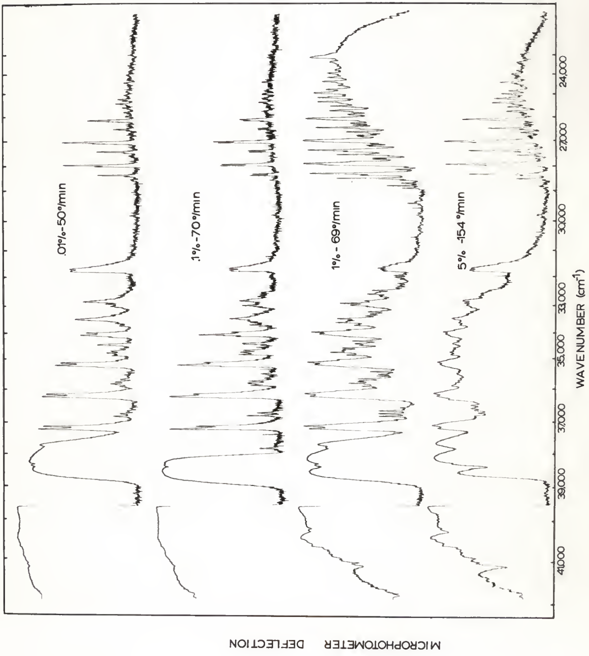
PLATE XII


3 deg/min
14 deg/min
60 deg/min
180 deg/min
H
L
H
L
H
L
24,000
27,000
30,000
33,000
35,000
37,000
39,000
41,000
WAVENUMBER (cm^{-1})
MICROPHOTOMETER DEFLECTION

EXPLANATION OF PLATE XIII

This plate is made from densitometer tracings of the spectrum of benzene in cyclohexane. The samples were all frozen rapidly to give the two phases. The tracings show variations in the emission with concentration.

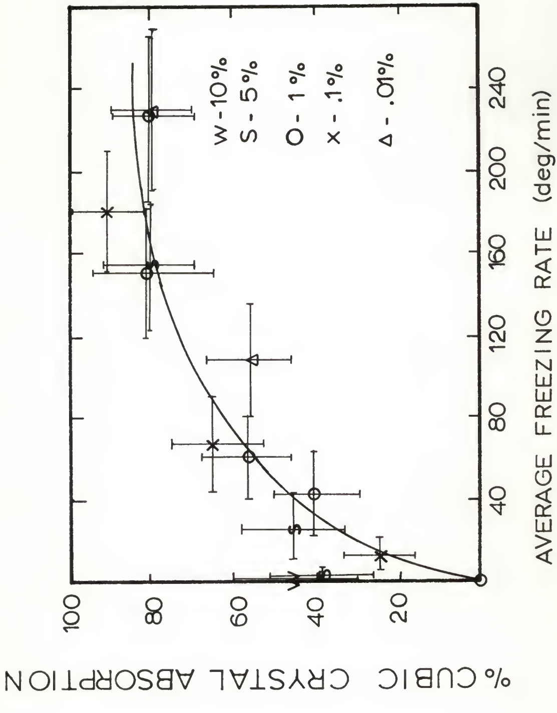
PLATE XIII


.01%-50°/min
.1%-70°/min
1%-69°/min
5%-154°/min
24,000
27,000
30,000
33,000
35,000
37,000
39,000
41,000
WAVENUMBER (cm^{-1})
MICROPHOTOMETER DEFLECTION

EXPLANATION OF PLATE XIV

A graph of the phase H absorption as a function of freezing rate and concentration. The plate shows that all the different concentrations result in the same curve.

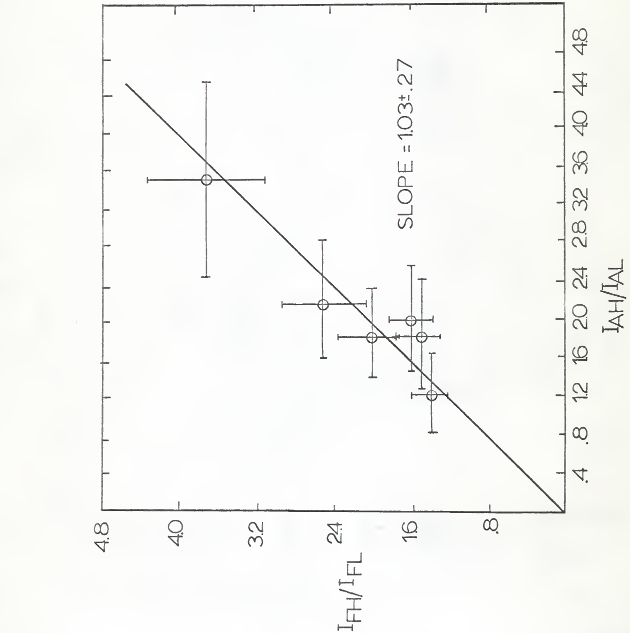
PLATE XIV


% CUBIC CRYSTAL ABSORPTION
100
80
60
40
20
AVERAGE FREEZING RATE (deg/min)
40
80
120
160
200
240
W - 10%
S - 5%
O - 1%
X - .1%
Δ - .01%

EXPLANATION OF PLATE XV

A graph of the ratio of the intensities for the absorption vs. the ratio of the intensities in the fluorescence. Each point on the graph comes from a different experiment. Each point is a result of the average of the ratio for several peaks in one spectrum. The concentration of the samples is .1 per cent.

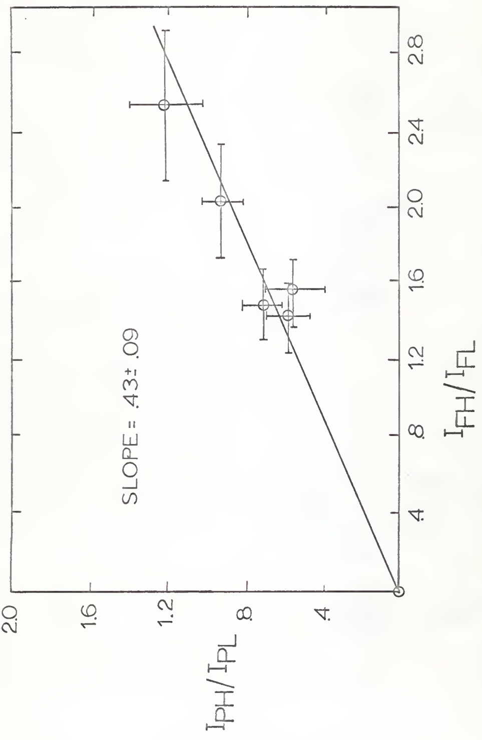
PLATE IV


SLOPE = 1.03±.27
I_{FH}/I_{FL}
4.8
4.0
3.2
2.4
1.6
.8
I_{AH}/I_{AL}
.4
.8
1.2
1.6
2.0
2.4
2.8
3.2
3.6
4.0
4.4
4.8

EXPLANATION OF PLATE XVI

A graph of the ratio of the intensities for the phosphorescence vs. the ratio of the intensities in the fluorescence. Each point on the graph comes from a different experiment. Each point is a result of the average of the ratio for several peaks in one spectrum. The concentration of the samples is .1 per cent.

PLATE XVI



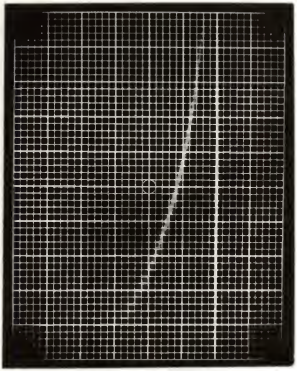
EXPLANATION OF PLATE XVII

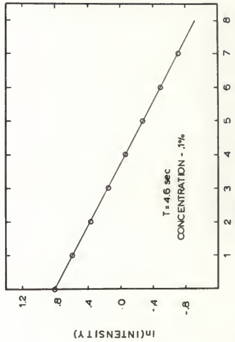
A picture of the intensity decay as shown on an oscilloscope trace accompanied by its logarithmic plot.

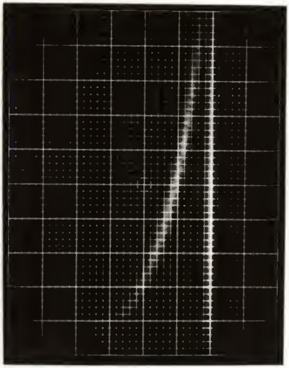
Fig. 1 The decay curve for a .01 per cent slow frozen sample with a sweep rate of 1 sec/cm and voltage sensitivity of .01 volts/cm.

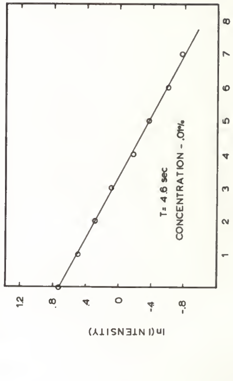
Fig. 2 The decay curve for a .1 per cent slow frozen sample with a sweep rate of 1 sec/cm and a voltage sensitivity of .02 volts/cm.

PLATE XVII




ln(INTENSITY)
1.2
.8
.4
.0
-.4
-.8
1
2
3
4
5
6
7
8
TIME (sec)
T= 4.6 sec
CONCENTRATION - .1%




ln(I NTENSITY)
1.2
.8
.4
0
-.4
-.8
1
2
3
4
5
6
7
8
TIME (sec)
T= 4.6 sec
CONCENTRATION - .01%

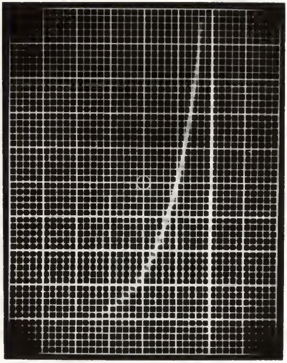
EXPLANATION OF PLATE XVIII

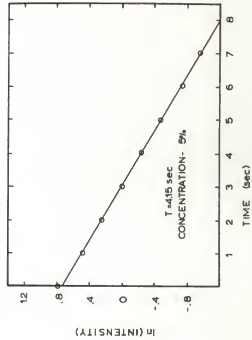
A picture of the intensity decay as shown on an oscilloscope trace accompanied by its logarithmic plot.

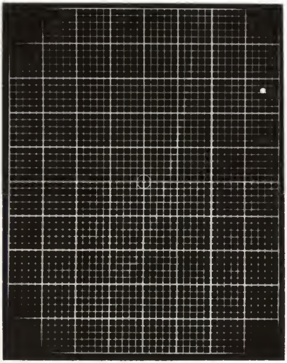
Fig. 1 The decay curve for a 1 per cent slow frozen sample with a sweep rate of 1 sec/cm and voltage sensitivity of .1 volts/cm.

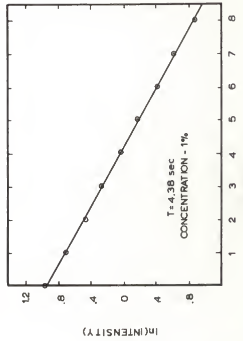
Fig. 2 The decay curve for a 5 per cent slow frozen sample with a sweep rate of 1 sec/cm and a voltage sensitivity of .02 volts/cm.

PLATE XVIII




T =4.15 sec
CONCENTRATION - 5%
ln (INTENSITY)
1.2
.8
.4
0
-.4
-.8
TIME (sec)
1
2
3
4
5
6
7
8

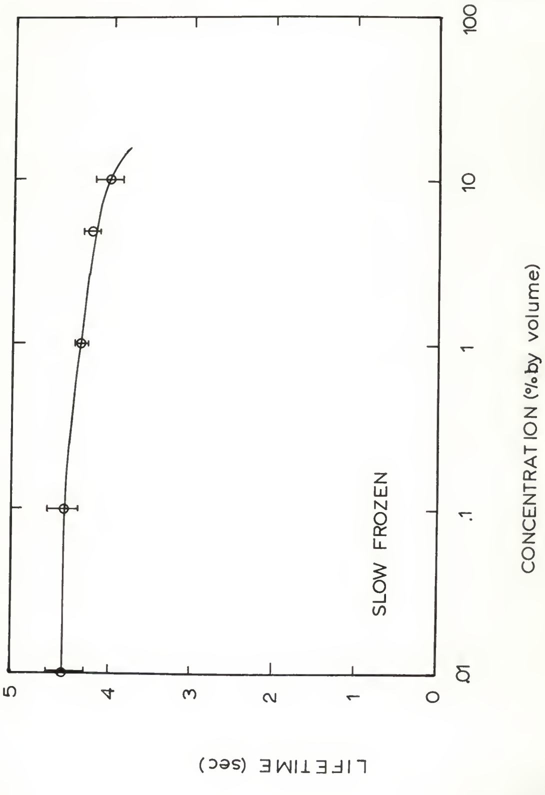



T = 4.38 sec
CONCENTRATION - 1%
ln(INTENSITY)
1.2
.8
.4
0
.4
.8
TIME (sec)
1
2
3
4
5
6
7
8

EXPLANATION OF PLATE XIX

A graph summarizing the lifetime measurements as a function of concentration for slow frozen samples.

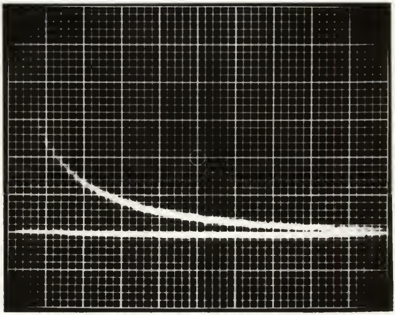
PLATE XIX

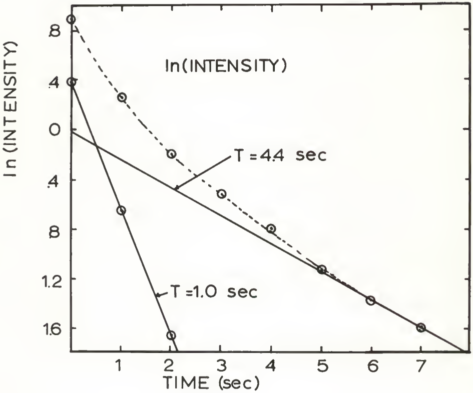

SLOW FROZEN
LIFETIME (sec)
CONCENTRATION (% by volume)
0
1
2
3
4
5
.01
.1
1
10
100

EXPLANATION OF PLATE XX

A picture of the intensity decay of a .1 per cent sample that was frozen rapidly accompanied by a plot of the ln(Intensity). The decay is analyzed as the sum of two decaying exponentials.

PLATE XX




.8
.4
0
.4
.8
1.2
1.6
In (INTENSITY)
In(INTENSITY)
T =4.4 sec
T =1.0 sec
1
2
3
4
5
6
7
TIME (sec)

DISCUSSION OF RESULTS

From the previous work on the absorption and phosphorescence, it was expected that the two crystal forms of cyclohexane would give rise to two identical fluorescence spectra; this was observed. It was also predicted that the intensities of the two spectra would depend on the freezing rate for the sample. Plate XIV shows that this was observed and that for absorption the same graph is obtained for different concentrations. The ratio of the absorption intensities will be equal to the ratio of the amounts of the two crystal forms present if the transition probabilities are equal for benzene in phase H and phase L. If the transition probabilities are not equal, then the ratio of absorption intensities will be proportional to the ratio of the amounts of the two crystal forms present. The conclusion is that the per cent of phase H present depends only on the freezing rate and not the concentration. This is reasonable first, because the concentrations used were low and second, because the benzene molecule has a similar size and shape and should fit into the cyclohexane lattice without causing severe distortions.

The emission intensities are expected to differ from the absorption if the rate constants for phase H and phase L are different or if there is energy migration taking place. From Plate XV the slope of the graph is 1.03 ± .2 per cent. In the section on theory, it was shown that the slope of the graph is equal to

$$\frac{k_{FL} + k_{ISCL}}{k_{FH} + k_{ISCH}} \; \frac{k_{FH}}{k_{FL}} \qquad (17)$$

Setting this equal to 1.0 yields after a little algebra

$$\frac{k_{ISCH}}{k_{ISCL}} \; \frac{k_{FL}}{k_{FH}} = 1 \qquad (18)$$

Leach, et al.[4], also note that the ratio of the intensities in the absorption and fluorescence are the same. This implies that they would also get 1.0 for the slope of the line. The coefficient has been reduced to the above expression because this product appears in the fluorescence-phosphorescence coefficient. From Plate XVI, the fluorescence-phosphorescence date gives .43 ± .09 for the slope. Using the expression derived in the theory section, equation (15), for the slope one has

$$.43 \pm .09 = \frac{k_{PH}}{k_{PL}} \frac{k_{FL}}{k_{FH}} \frac{\tau_H}{\tau_L} \frac{k_{ISCH}}{k_{ISCL}} \tag{19}$$

Using the result of equation (18), one obtains

$$.43 \pm .09 = \frac{k_{PH}}{k_{PL}} \frac{\tau_H}{\tau_L} \tag{20}$$

or

$$\frac{k_{PH}}{k_{PL}} = (.43 \pm .09) \frac{\tau_L}{\tau_H} \tag{21}$$

From the lifetime studies for this thesis, τ_L = 4.6 sec ± .1 sec and τ_H = 1.1 sec ± .2 so

$$\frac{k_{PH}}{k_{PL}} = 1.8 \pm .7 \tag{22}$$

There is likely little effect of the environment on the process involving the singlet state, and k_{ISC} and k_F are probably the same in both phases. The results for the phosphorescence, however, suggest that there is an environmental effect on the rate constants. The lifetime studies indicate there is definitely a greater rate of depopulation of the triplet state for phase H and the above result, equation (22), suggests that the rate constant for phosphorescence is approximately two times as large for benzene in phase H as for benzene in phase L.

It has been assumed in the past that there is a natural radiative lifetime for benzene of about 26 seconds[26] and that the decrease in lifetime in various solvents is due wholly to an increase in radiationless processes. This work suggests that both radiation and radiationless rate constants are affected by the environment and that as one increases so does the other. It is possible though that there is a larger error somewhere than is apparent and that the ratio of k_{FH}/k_{FL} is equal to 1.

The above results are for concentrations of 0.1 per cent and 0.01 per cent. At concentrations above 1 per cent, there is more emission from the L phase than should be assigned to the differences in rate constants. Robinson, et al.[26,31], indicate that energy transfer should be efficient at this concentration, and results from this investigation agree with this. It is very difficult to make a quantative comparison with Robinson's theory of energy transfer because the theory contains so many unknown parameters and the size of the regions of the crystal that are phase H and phase L are unknown.

Lifetime Data

The lifetime (4.6 seconds) determined here is similar to what other people have obtained in similar solvents. McClure[27] gives 7 seconds for Benzene in EPA and Hirayama[5] gives 6 seconds. Russel and Albrecht[28] give 5.2 seconds in 3 methyl pentane. Kanda and Shimoda[29] give approximately 5 seconds in p-dioxane. Hirayama[5], however, in his graph of lifetime versus concentration, shows 2 seconds for low concentrations of benzene in cyclohexane and about 4 seconds for concentrations of above 5 per cent. He suggests that this peculiar variation with concentration might be related to the two crystal forms of cyclohexane. The way Hirayama froze his sample was by putting it in a 3 mm i.d. quartz tube and immersing it in liquid nitrogen.

This process would likely freeze the sample quite rapidly. His lifetime measurement would then be a combination of the 1.1 and 4.6 second decays. From experiments used for this thesis with fast frozen samples, the decays can be analyzed as the sum of two exponentials with 1.1 and 4.6 second lifetimes. The time for the intensity to decay to 1/e times its initial value is approximately two seconds, which is what Hirayama gives. The increase of the lifetime with increasing concentration can be explained by energy transfer. Triplet-triplet migration occurs until the energy is trapped in a portion of the crystal that is in phase L, which has approximately a 4 second lifetime. The ratio of the intensity of the phosphorescence to the intensity of the fluorescence as measured by Hirayama remains constant up to about 10 per cent, which indicates that the energy absorbed by phase H is not lost in radiationless transitions but must be transferred to phase L as indicated by the lifetime.

If one compares the lifetime data determined in this study for slow frozen samples with Hirayama's ratio of I_P/I_F, one sees that the ratio begins to decrease at the same place as the lifetime does. This result is the same as he obtained for benzene in EPA. His conclusion about benzene in EPA was that "triplet-triplet energy migration occurs with increased efficiency enhancing radiationless transitions." Thus, the conclusion is that for 5 per cent concentrations of benzene in cyclohexane, energy transfer is very efficient and at 10 per cent the radiationless processes are starting to increase with concentration.

Wavelength Measurements

A comment can be made about the third (0, 0) level that Sponer, et al.[1] used in their analysis of the phosphorescence. Satellite bands displaced approximately 35 cm^{-1} from the strong lines also appear in the fluorescence and absorption. The satellite bands are somewhat diffuse, but one can clearly see them on the (0, 0) band in the fluorescence and the absorption. In the absorption, the satellite bands appear on the higher energy side of the strong band they accompany, and in the fluorescence they appear on the lower energy side. This can be seen on Plate XI. The placement of the bands rules out the possibility of yet a third environment, which was suggested by Sponer. The appearance on the higher energy side of the strong bands in the absorption and the lower energy side in the fluorescence suggests some kind of vibration, but all the vibrations of the benzene molecule are well accounted for, and the lowest is approximately 400 cm^{-1} in the ground state and 220 cm^{-1} in the first excited singlet state. The only alternative at present seems to be to attribute the satellite bands to lattice vibrations. The bands increase in intensity at higher temperatures. In the absorption the bands appear at 35 cm^{-1}, 70 cm^{-1}, and 105 cm^{-1} to the higher energy side of some of the peaks. The fluorescence shows satellite bands at approximately 40, 80, and 148 cm^{-1} from the strong bands. The uncertainty in the measurements is 5 to 10 cm^{-1} because the bands are diffuse. Because of the uncertainty, one cannot rule out the possibility that they are all the same fundamental lattice vibration of about 35 cm^{-1}.

Leach[4] also observes the 148 cm^{-1} band (he measures it as 144 cm^{-1}) and claims at higher temperatures to see also 2X144 cm^{-1}, 3X144 cm^{-1}, and 4X144 cm^{-1} coupled to the fluorescence. In this study the bands 2X144 cm^{-1} and 3X144 are seen only as very weak bands on the highest intensity plate. The band at 4X144 cm^{-1} is stronger. However, some caution must be used in claiming these are due to lattice vibrations. Three times 144 cm^{-1} = 432 cm^{-1}, which when added to 607 cm^{-1} gives a displacement of 1039 cm^{-1}

from the (0, 0) band. There is a ground state vibration of 1037 cm^{-1}, though its appearance as a fundamental in the fluorescence is forbidden by symmetry. Four times 144 cm^{-1} = 576 cm^{-1} which when added to 607 cm^{-1} gives 1183 cm. This is very close to the 1176 cm^{-1} e_g + vibration, which is allowed by symmetry: an interpretation in terms of this vibration seems much more likely. Some of the plates taken in this study show a large number of weak bands, and it is expected that some of these will be lattice vibrations coupled to other bands when the analysis is complete.

SUMMARY

By studying the relative intensities of the H and L band systems, it was possible to learn several things. First, the percentage of phase H lattice form present appears to depend only on how fast the sample is frozen. Second, the variation with concentration that was suggested by Spangler and Sponer[2] cannot explain the phosphorescence results. These results are attributed to changing rate constants. The rate constant that changes most with concentration is the rate constant for energy transfer. The radiationless transition rate constants may be enhanced with increasing concentration too, but up to 10 per cent this does not seem to be a large factor. At 10 per cent radiationless transitions appear to begin to increase with concentration. Third, the relative intensities of H and L bands in absorption and fluorescence for low concentrations are the same. From this, it is possible to deduce that the rate constants for intersystem crossing are the same in both crystal phases as well as the rate constants for fluorescence. Fourth, the relative intensity measurements for concentrations approximately greater than 1 per cent can be explained best by a theory of energy transfer such as that developed by Robinson. At concentrations of approximately 5 per cent this energy transfer must be very efficient.

For slow frozen low concentration samples, the data shows a 4.6 second lifetime. The decays are exponential and all the points lie within the experimental error of the measurements. At 10 per cent the first point does not lie on the line, but at this concentration so much energy transfer is taking place that any minute amount of impurity or imperfection will be an efficient emitter. The decays of fast frozen 0.1 per cent samples can be analyzed as the sum of two exponentials with 1.1 and 4.6 second lifetimes. The 1.1 second lifetime is attributed to phosphorescence from the H lattice.

Further research in several areas could prove profitable. It would be interesting to do the experiments on relative intensity with more accuracy, using photoelectric rather than photographic detection, so that one could determine with more certainty which rate constants would depend on the environment. From the experiments for this study, it seems that the intersystem crossing and fluorescence rate constants are the same for both lattices. This could be verified with more accurate data. Also, the data indicates that the radiationless transition rate constants for the T_1 to S_0 transitions in the two lattices are different, and the same may be true for the phosphorescence rate constants, k_{PH} and k_{PL}. It has generally been thought that there is a natural radiatime lifetime of about 26^{26} seconds and that k_p is .0388 sec^{-1}, independent of the environment. More accurate relative intensity measurements could clarify this point. Varying the temperature could prove fruitful in further determining the processes and their relative importance. Doing the experiments with deuterated benzene would be interesting because radiationless transitions are significantly decreased.[26]

Appendix A

Suppose it is necessary to consider energy transfer from phase H to phase L as shown in Fig. 5.

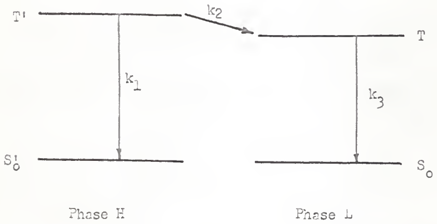


Fig. 5

Let N' and N be the population T' and T respectively.

$$\frac{dN'}{dt} = -(k_1 + k_2)N' \tag{1}$$

$$N' = N_o'e^{-(k_1 + k_2)t} \tag{2}$$

For the T state

$$\frac{dN}{dt} = +k_2N' - k_3N \tag{3}$$

Substituting from (2)

$$\frac{dN}{dt} = k_2N_o'e^{-(k_1 + k_2)t} - k_3N \tag{4}$$

Multiplying (4) through by e^{+k_3t}

$$\frac{dN}{dt}\, e^{+k_3t} + k_3Ne^{+k_3t} = k_2N_o'e^{-(k_1 + k_2 - k_3)t} \tag{5}$$

Integrating (5) gives

$$Ne^{k_3t} = \frac{-k_2N_0'}{k_1 + k_2 - k_3} e^{-(k_1 + k_2 - k_3)t} + C \qquad (6)$$

Multiplying through by e^{-k_3t} gives

$$N = \frac{-k_2N_0'}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)t} + Ce^{-k_3t} \qquad (7)$$

Setting $t = 0$ implies

$$N_0 = C - \frac{k_2N_0'}{k_1 + k_2 - k_3} \qquad (8)$$

Substituting (8) in (7) gives

$$N = \frac{-k_2N_0'}{k_1 + k_2 - k_3} e^{-(k_1 + k_2)} = (N_0 + \frac{k_2N_0'}{k_1 + k_2 - k_3})e^{-k_3t} \qquad (9)$$

The phototube response will be

$$I = -\frac{dN}{dt} - \frac{dN'}{dt} \qquad (10)$$

which is

$$I = +k^3(N_0 + \frac{k_2N_0'}{k_1 + k_2 - k_3})e^{-k_3t} + \frac{(k_1 + k_2)(k_1 - k_3)}{(k_1 + k_2 - k_3)} N_0e^{-(k_1 + k_2)t} \qquad (11)$$

When $k_2 \gg k_1$ and k_3, this gives $N_0' = 0$ and $I = k_3N_0e^{-k_3t}$.

Thus, for the case where efficient triplet-triplet energy migration occurs, the intensity will decay exponentially and the lifetime will be that of phase L.

EXPLANATION OF PLATE XXI

A computer program for determining the wavelengths and wavenumbers of unknown lines using the Hartmann Dispersion Formula and the Cauchy Index of Refraction of Air.

PLATE XXI

```
               FORTRAN LISTING             1410-FO-970                   05297                   PAGE  001
      OIMENSIONWLFE(9),WNFE(9),OFE(9)
00001 FORMAT(I4)
00003 FORMAT(1H1,60X,12HPLATE NUMBER,I3//)
00004 FORMAT(I4/(2F10.2,F10.4))
00005 FORMAT(14HLPRINT NUMBER  ,I4//15H LAMBOA ZERO =  ,F8.2,5X,4HC = ,   F15.2,5X,13HD ZERO BAR = ,F8.2//)
00006 FORMAT(6H   IRON,20X,10HCALCULATED,35X,10HCALCULATED)
00007 FORMAT(6H   LINE,5X,10HWAVELENGTH,5X,10HWAVELENGTH,5X,10HCORRECTION,5X,10HWAVENUMBER,5X,10HWAVENUMBER,5X,1
          CHCORRECTION)
00008 FORMAT(I6,6F15.2)
00009 FORMAT(F10.4,A6)
00010 FORMAT(6HL LINE,5X,10HWAVELENGTH,5X,10HWAVENUMBER,6X,4HCODE)
00011 FORMAT(1HK,I6,2F15.2,4X,A6)
      READ(1,1)NN
      DO102K=1,NN
      READ(1,1)IPLT
      WRITE(3,3)IPLT
      READ(1,1)N
      DO102II=1,N
      REAO(1,4)L,(WLFE(I),WNFE(I),CFE(I),I=1,9)
      A=(OFE(5)-DFE(1))/(WLFE(5)-WLFE(1))
      AB=A-(DFE(9)-DFE(1))/(WLFE(9)-WLFE(1))
      COO=(DFE(9)-DFE(5))/AB
      WLO=WLFE(1)-CDO
      ODC=A*(WLFE(5)-WLO)
      C=COO*DOO
      OOB=OOO+DFE(1)
      WRITE(3,5)II,WLO,C,DOB
      WRITE(3,6)
      WRITE(3,7)
      DO99J=1,9
      WLCAL=WLO+C/(DOB-OFE(J))
      WNCAL=ENVER(WLCAL)
      CORL=WLFE(J)-WLCAL
      CORN=WNFE(J)-WNCAL
      WRITE(3,8)J,WLFE(J),WLCAL,CORL,WNFE(J),WNCAL,CORN
00099 CONTINUE
      WRITE(3,10)
      DO102J=1,L
      READ(1,9)DX,CODE
      WL=WLO+C/(OO8-OX)
      WN=ENVER(WL)
      WRITE(3,11)J,WL,WN,CODE
00102 CONTINUE
      STCP
      ENC
      FUNCTIONENVER(A)
      R=1.0+(2726.43+(12.288/(A*A))*1.0E8+(0.3555/A**4)*1.0E16)*1.0E-7
      ENVER=1.0E8/(A*R)
      RETURN
      ENO
```

ACKNOWLEDGMENT

The author takes this opportunity to acknowledge and thank Dr. J. D. Spangler for his guidance and assistance in this work. The author wishes to thank Dr. A. B. Cardwell, Head of the Department of Physics, and the National Science Foundation for their financial assistance.

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NEAR ULTRAVIOLET SPECTRA OF BENZENE IN FROZEN CYCLOHEXANE SOLUTIONS

by

NELSON GLENN KILMER

B. S., Goshen College, 1963

AN ABSTRACT OF A MASTER'S THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Physics

KANSAS STATE UNIVERSITY
Manhattan, Kansas

1967

The absorption, fluorescence, and phosphorescence of mixed crystals of benzene in cyclohexane have been studied. Cyclohexane undergoes a solid-solid phase change at 186°K. Only part of the cyclohexane changes phase if the sample is frozen rapidly. The presence of two crystal forms of cyclohexane results in two identical benzene spectra separated by 83 cm^{-1} in the absorption and fluorescence and 59 cm^{-1} in the phosphorescence.

The relative intensities of the two spectra have been measured as a function of freezing rate and concentration. It is shown that the relative intensities of the absorption do not agree with the relative intensities of the emission. The relative intensities of the absorption are shown to be dependent primarily on the freezing rate, while the relative intensities in the emission are dependent on both concentration and freezing rate. Energy transfer is suggested as being partially responsible for the increased emission from the low energy spectrum.

The measured lifetime of the phosphorescence from a slow frozen low concentration sample is 4.6 seconds. Fast frozen samples give intensity decays that can be analyzed as the sum of a 4.6 second exponential decay and a 1.1 second exponential decay. The shorter lifetime indicates a larger rate constant for radiationless transitions. This partially explains the decrease in phosphorescent intensity from the high energy spectrum.

Wavelength measurements show activity of lattice vibrations of approximately 35 cm^{-1} in the absorption and 40, and 148 in the fluorescence.